COST OPTIMIZATION OF NEUTRALIZING AMINES USED IN DISTILLATION COLUMN OVERHEAD SYSTEMS

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Received: 16.10.2018 / Revised: 25.11.2018 / Accepted: 10.04.2019 / Published on line: 18.06.2019

ABSTRACT

Crude distillation equipment is usually subject to the corrosive activity of acids. This problem could be mitigated by the addition of amines to reduce corrosion effects. The present work applies two different optimization methods, Nelder-Mead (NM) and Particle Swarm Optimization (PSO), to reduce operational costs by adding neutralizing amines. This improvement was accomplished using an in-house software taking into account the following parameters: salt formation temperature, water dew point temperature, and pH in condensate vessel conditions. These operating parameters and the addition of amines were used to minimize the cost in four different case studies. Results show that a considerable cost reduction is possible in several cases when using the global optimization method. Nevertheless, the local search method was less successful in improving the given start point, getting stuck in local minima.

KEYWORDS

crude oil; distillation; amines; optimization; corrosion

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doi:10.5419/bjpg2019-0007

1. INTRODUCTION

The process of refining crude oil through distillation is very important in the production of various oil-based components and products. These products are used widely in our daily lives; among them are gasoline, kerosene, and diesel. Heavier fractions, which have a higher boiling point, are collected in the tower bottoms, while lighter fractions, which present lower boiling point, are recovered from the overhead fraction (Fearnside & Murphy, 1995).

Typically, the first approach to reduce corrosion on the overhead section is to promote oil desalting with water (Fearnside & Murphy 1998). However, no matter what type of petroleum feedstock is used, it is usually impractical to remove the salts completely (Branden et al., 1999). These salts hydrolyze in the pre-heat stage and the distillation equipment ends up subjected to the corrosive activity of acids such as H_2S , HCl , H_2CO_3 and organic acids, as water condenses in the overhead section (Branden et al., 1999).

Furthermore, steam is added to the bottom of the tower to promote stripping of light compounds from the bottom. Water can also be added to the top of the column to wash salts away. The amount of water added to the system is usually substantial, making the top stream reach values of 40% (molar basis) in water. All water is condensed in the overhead exchangers and is temporarily accumulated in the condensate drum (Branden et

al., 1999). Because of the water temperature is close to its dew point, the temperature variation that occurs during the phase change of the condensing mixture increases the chance of a corrosive attack by acid species. Other possibility of corrosive attack may occur when acidic species react further in the gas phase with ammonia/amines (e.g. NH_3) and salt formation occurs (e.g. NH_4Cl). Depending on operating conditions, salts may form at a temperature higher than the water dew temperature. When these salts precipitate, they may form a deposit on the internal surface of the equipment, triggering corrosion processes, and, in turn, causing great damages to the equipment and considerable financial losses (Lehrer & Edmondson, 1993).

The top systems of distillation towers are also called OVHD - Overhead Gutzeit (2006). Differently from the amine injection method presented by Branden et al. (1999), Gutzeit (2006) suggests the addition of amines and inhibitors to the top of the towers along with the washing water, according to Figure 1.

Neutralizing amines are considered weak bases when applied to tower systems. They play a key role in the corrosion inhibition as they can neutralize the acidic species present. This increases the pH value making the mixture less acidic in top systems. To minimize the corrosion in the system, the pH range should be about 5 to 6.5 (Branden et al., 1999; Gutzeit, 2006).

Figure 1. Schematic representation of the OVHD system investigated in this work Cases. adapted from (Gutzeit, 2006).

The main goal of adding amines to the process is to promote the neutralization of acidic species. The inhibitors, on the other hand, form a protective film between the internal surface of the equipment and the mixture of the medium, through chemical adsorption or electrostatic forces, protecting them from corrosive attacks (Neves, 2009).

In the OVHD system of distillation processes, there are three main operational parameters to consider: salt formation temperature, water dew point temperature, and pH in the condensate vessel. The salts formed by precipitation generally are detected during the distillation of crude oil at the beginning of the first stage of condensation. At the lower levels of the fractionating column (high temperatures), sulfur compounds can be decomposed to form salts such as ammonium hydrosulfide (NH_4HS) and nitrogen compound. These compounds might react with hydrochloric acid to form salts like ammonium chloride (NH_4Cl). The formation of these salts depend on the equilibrium constants and the partial pressures of the components in mixture (McLaughlin and Wu, 1997).

Water dew point temperature is obtained assuming that the water will condensate practically pure, considering only gases dissolved in small amounts or slightly miscible oils. Water dew point temperature can be calculated through its total and partial pressures relative to its saturation pressure, applying the modified Raoult's law and the Antoine equation, respectively (Koretsky, 2012).

The pH of the top vessel, as well as the pH of the water, can be determined by the dissociation of water and acidic species and their respective equilibrium constants along with material balances.

The process of adding neutralizing amines to accomplish corrosion control represent an operating cost. In this work, with the objective of reducing the costs associated with the corrosion control by amine addition, two optimization methods were used: a local search method (Nelder-Mead simplex) and a global search method (Particle Swarm Optimization - PSO). These methods were implemented in an in-house software developed by our group.

2. METHODOLOGY

2.1 Operational parameter calculations

An adequate pH of the aqueous phase is crucial to reduce corrosion effects. In this work, the pH of the aqueous phase in the distillate vessel is used as an operational parameter. Two other parameters are also considered: the water dew point temperature and salt formation temperature.

The prediction of these operational parameters were implemented in an in-house software developed by our group. Besides interactions with ammonia (NH_3), the implementation also supports its mixture with the following amines: 3-Methoxypropylamine (MOPA), Monoethanolamine (MEA), N-Methylmorpholine (NMM), Trimethylamine (TMA), Ethylenediamine (EDA), and Pyridine (PYRID). Along with the computation of the operational parameters, given the cost of each amine, the software can also compute the current operational cost for the current selected neutralizing mixture. Finally, given the operational conditions, the code can optimize the composition of the neutralizing mixture to achieve an optimal (minimum) operating cost.

During the optimization step, the following constraints need to be applied: the pH in condensate vessel should be higher than 6.5 and salt formation temperature should be lower than the water dew point temperature.

2.1.1 Water dew point temperature

Assuming that the aqueous phase is practically pure water, the water dew point temperature can be calculated by its partial pressure relative to its saturation pressure (McLaughlin and Wu, 1997). Starting from the modified Raoult's law:

$$Py_i = x_i \gamma_i P_i^{sat}(T) \quad (1)$$

Where:

P = pressure of system;

y_i = the molar fractions in vapor phases;

x_i = the molar fractions in liquid phases;

γ_i = the activity coefficient of the species i ;

P_i^{sat} = the saturation pressure of compound i .

Furthermore, the aqueous liquid phase (if present) is assumed to be pure water. Thus, the product $x_i \gamma_i$ reduces to 1, simply resulting in:

$$P_{H_2O}^{sat}(T) = y_{H_2O} P \quad (2)$$

Where:

$P_{H_2O}^{sat}$ = saturation pressure of water;

y_{H_2O} = molar fractions in vapor of water;

P = pressure of system.

Thus, the temperature dew point of water can be calculated for given operational conditions (P and y_{H_2O}) using a temperature dependent correlation for $P_{H_2O}^{sat}$. In this work, the Antoine equation was used:

$$\ln(P^{sat} [bar]) = A - \frac{B}{T + C} \quad (3)$$

Where:

$P^{sat} = P_{H_2O}^{sat}$: saturation pressure of water;

A, B, C = empirical constants of Antoine equation for water;

$T = T_{H_2O}$ = water dew point temperature.

2.1.2 Salt formation temperature

The amines could form hydrochloride salts. The salt formation temperature will be exemplified in this section using ammonium hydrochloride, as follows:

Assuming solid-vapor equilibrium, that the solid phase is pure, and that vapor phase is an ideal gas (low pressures), the equilibrium constants can be related to the partial pressures by:

$$K_1(T) = P_{NH_3} P_{HCl} \quad (4)$$

Where:

K_1 = equilibrium constant for salt 1 (NH_4Cl);

T = temperature;

$P_{NH_3} = P y_{NH_3}$ = partial pressures of NH_3 ;

$P_{HCl} = P y_{HCl}$ = partial pressures of HCl .

Equation 4 allows one to represent the equilibrium constants through the molar fractions and total system pressure (McLaughlin & Wu 1997):

$$K_1(T) = P^2 y_{NH_3} y_{HCl} \quad (5)$$

Where:

P = operating pressure;

y_{NH_3} = molar fractions of NH_3 ;

y_{HCl} = molar fractions of HCl .

Equilibrium constant K_1 can be obtained based on pure salt sublimation pressure data. When the pure salt sublimates, vapor is an equimolar mixture of NH_3 and HCl with $y_{NH_3} = y_{HCl} = 0.5$. Thus, Equation 5 reduces simply to:

$$K_1(T) = 0.25 P_{subl}^2 \quad (6)$$

Where:

P_{subl} = sublimation pressure of the salt.

Where P_{subl} is a function of temperature only. The equilibrium constant determined by Equation 6 can also be translated into the Gibbs free energy of reaction as follows:

$$\ln K_1(T) = - \frac{\Delta g_{rxn}^\circ}{RT} \quad (7)$$

Where:

Δg_{rxn}° = Gibbs free energy of reaction;

R = ideal gas constant.

Furthermore, assuming that the enthalpy of reaction (or sublimation) is constant, the following equation can be used to extrapolate the constant for different temperatures:

$$\ln K_1(T_2) = \ln K_1(T_1) - \frac{\Delta h_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (8)$$

Where:

Δh_{rxn}° = reaction enthalpy of formation;

T_1 = reference salt temperature;

T_2 = salt temperature to be determined.

Table 1. Salt formation equilibrium constants as well as pKa data for ammonia and amines.

Amine Salt	P_{subl} (Pa)	Δg_{rxn}° (kJ/mol)	Ref.Temp (K)	pKa
NH ₃ - HCl	0.0021[1]	91.420	298.15	9.21[6]
MOPA - HCl	1.0700[2]	75.192	372.04	10.3[7]
MEA - HCl	1.0700[2]	75.192	372.04	9.44[8]
NMM - HCl	0.9380[3]	77.041	377.59	7.14[5]
TMA - HCl	70.000[4]	52.930	400.00	9.76[6]
EDA - HCl	0.0038[5]	176.620	380.37	10.7[5]
PYRID - HCl	45.600[5]	52.657	377.59	5.25[5]

[1](Callanan and Smith, 1971), [2](Fearnside and Murphy, 1998), [3](Lehrer and Edmondson, 1993) [4](Belusso et al., 2017), [5](Lehrer and Edmondson, 1993), [6](Hall, 1957), [7](Brown et al., 1971), [8](Hamborg & Versteeg 2009)

Therefore, by using P_{subl} data of the amine salts, it is possible to determine Δg_{rxn}° and Δh_{rxn}° . To obtain Δh_{rxn}° , sublimation pressure data, at least two different temperatures are needed. For some amines, data for only one temperature is available in the literature, making it impossible to determine the sublimation enthalpy value. However, these enthalpy data are usually very similar for different amines, thus, the NH_4Cl value of $\Delta h_{rxn}^\circ = 176.340$ kJ/mol (Callanan & Smith, 1971) was assumed for all amines in this work, except for the EDA salt. Since the EDA salt contains 2 HCl molecules, an $\Delta h_{rxn}^\circ = 352.680$ was assumed. The required data for the amines investigated are listed in Table 1. The data for ionization constants (pKa) are also listed in Table 1.

2.1.3 pH calculation

2.1.3.1 Water pH

In the calculation of water pH, concepts of ionization and equilibrium constants are used. Water has a high polarity and, in liquid phases, it becomes slightly ionized. That ionization can be represented by the following reaction:

Therefore, it is possible to represent the above reaction in terms of its equilibrium constant:

$$K_{a,W} = \frac{a_{H^+} a_{OH^-}}{a_W} = \frac{M_{H^+} M_{OH^-}}{M} \quad (9)$$

Where:

$K_{a,W}$: equilibrium constant of water;

a_i : species activity ionic representations;

M_i : molal concentrations.

With $K_{a,W}$ it is possible to calculate the ionization constant ($pK_{a,W}$) through the relation.

$$pK_{a,W} = -\log_{10}(K_{a,W}) \quad (10)$$

In a similar way, the pH is defined as:

$$pH = -\log_{10}(a_{H^+}) \quad (11)$$

2.1.3.2 pH in condensate vessel conditions

The pH in the condensate vessel represents the calculation of the acidity of the condensate, consisting of water, amines, and acidic species. Thus, this pH can be calculated through the solution of simultaneous acid-base reactions of all species present. To all bases, using NH_3 as an example, the following reaction is considered:

And for acids, taking HCl as an example:

Each of these reactions presents an associated equilibrium constant. A set of equations involving all acids and bases present in the solution must be solved simultaneously to determine the H^+ concentration. Thus, Equation 11 allows pH calculation.

Table 2. Assumed specific cost and density of ammonia and amines.

Amines	Temperature Amines (°C)	ρ (kg/L)	US\$/ton
NH ₃	20	0.900 [12]	430 [9]
MOPA	25	0.874 [12]	3100 [10]
MEA	25	1.012 [12]	1700 [9]
NMM	25	0.920 [12]	3910 [11]
TMA	20	0.630 [12]	887 [11]
EDA	25	0.899 [12]	1730 [10]
PYRID	25	0.978 [12]	2400 [9]

[9](ALIBABA.COM 2016), [10](FOCUS TECHNOLOGY CO. 2016),
[11](MOLBASE 2016), [12](SIGMA-ALDRICH 2016).

Table 3. Required input data for the case studies investigated in this work.

OVHD System	Data	Case 1	Case 2	Case 3	Case 4
Feed and Reflux	Feed (m ³ /h)	1000.00	1000.00	1000.00	1000.00
	Water (%)	0.00	0.00	0.00	0.00
	Total Steam (ton/h)	2.46	4.00	4.00	4.00
	Reflux (m ³ /h)	50.67	100.75	90.75	100.75
Tower Top	Temperature (°C)	105.00	127.00	127.00	127.00
	Pressure (kgf/cm ²)	1.90	1.10	2.72	1.10
	Flow (L/h)	1.00	1.00	1.00	1.00
Condensed Vessel	Temperature (°C)	50.00	55.00	58.80	55.00
	Chlorides (ppm)	122.00	47.00	11.00	47.00
	Ammonia (ppm)	0.00	31.00	3.10	0.00
	Remaining water (ton/h)	5.00	5.00	5.00	5.00
	Sulfides (ppm)	13.00	6.00	13.00	6.00
	Organic acids (ppm)	23.00	15.00	5.70	15.00
Naphtha	Flow rate (m ³ /h)	16.00	8.00	10.00	8.00
	SG (kgf/cm ²)	0.76	0.69	0.69	0.69
Naphtha distillation curve (ASTM D86 Method)	0%	29.10	25.00	25.00	25.00
	10%	50.70	30.00	30.00	30.00
	30%	68.40	45.00	38.00	45.00
	50%	82.00	95.00	78.70	95.00
	70%	92.30	125.00	107.90	125.00
	90%	107.20	145.00	136.54	145.00
	100%	121.10	185.00	185.00	185.00

2.2 Cost and properties of amines

For the calculation of the operating costs and properties, assumed amine quotations as listed in Table 2.

All amines listed in Table 2 are used commonly in distillation towers, generally in aqueous solution (Lehrer & Edmondson, 1993). The TMA is an exception compared to the rest of the amines, since it has a high vapor pressure. This may pose

additional difficulties for its practical use (Felsing & Phililips, 1936).

3. RESULTS E DISCUSSIONS

This section presents the optimization results of four different cases. All cases studied present different input data, aiming to cover typical conditions observed in Brazilian refineries.

3.1 Case studies

This work investigates four case studies, with different operating conditions. Required input data for these cases are listed in Table 3. Neutralization is obtained by the addition of amines (NH_3 , MOPA, MEA, NMM, TMA, EDA, and PYRID) given by their total flow (L/h). Different optimization results for each case are listed on Tables 4, 5, 6, and 7. These tables provide resulting individual amine flow rates (L/h) as well as volumetric fractions (%). The operational cost (US\$/h) is the objective function, given by $\sum_{i=1}^i CA_i FA_i$, where (FA_i) is the total flow of the amine, and i (L/h) and (CA_i) are the specific cost (US\$/L).

For each case, different scenarios were investigated. First, two mixture compositions were selected randomly as candidates for operation (indicated as Mixture 1 and Mixture 2 in Tables 4-7). These mixtures represent the typical trial and error present in the empirical product formulation. With the compositions fixed (volume fractions),

only the total flow was optimized to respect operational constraints (dew point, salt point, and pH). Thus, Mixture 1 and Mixture 2 results will always be sub-optimal.

Afterwards, with Mixture 1 and Mixture 2 results set as initial point, the local search method (NM) was used to optimize the conditions, leading to the conditions identified as Optimization 1 NM and Optimization 2 NM, respectively. Finally, a global optimization (PSO) was also executed for each case, with results identified as Optimization PSO.

3.1.1 Case 1

With the input data of Table 3 for Case 1, the operational parameters and the optimized cost of were calculated, with results listed in Table 4.

Mixtures 1 and 2 represent typical trial and error formulation with a total flow that satisfies operating constraints.

Table 4. Optimization results for Case 1.

Optimization Variables			Operational Parameters						
	Amines	Flow	%	Water Flow	Water Dew	Salt Formation	pH	Cost	Time
		(L/h)		(m ³ /h)	Point (°C)	Point (°C)	OVHD	(US\$/h)	(ms)
Mixture 1	TMA	0.86	50.00						
	PYRID	0.86	50.00						
	TOTAL	1.72	100.00	11.55	98.36	91.79	6.500	2.490	-
Optimization 1 NM*	NH ₃	0.07	5.46						
	MOPA	0.09	6.93						
	MEA	0.05	4.34						
	TMA	0.50	39.39						
	EDA	0.06	4.48						
	PYRID	0.50	39.40						
	TOTAL	1.27	100.00	11.55	98.36	91.79	6.500	1.898	865
Mixture 2	NH ₃	0.10	5.00						
	TMA	0.76	40.00						
	PYRID	0.29	15.00						
	WATER	0.76	40.00						
	TOTAL	1.91	100.00	11.55	98.36	95.35	6.500	1.140	-
Optimization 2 NM*	NH ₃	0.13	14.30						
	NMM	0.04	4.80						
	TMA	0.43	48.50						
	EDA	0.12	13.76						
	PYRID	0.17	18.64						
	TOTAL	0.89	100.00	11.55	98.36	95.35	6.500	1.028	2117
Optimization PSO**	NMM	0.88	100.00						
	TOTAL	0.88	100.00	11.55	98.36	97.52	6.500	0.341	4965

*NM: Nelder-Mead simplex numerical method. **PSO: Particle Swarm Optimization numerical method.

Table 5. Optimization results for Case 2.

Variables of Optimization		Operational Parameters							
	Amines	Flow	%	Water Flow	Water Dew Point	Salt Formation Point	pH	Cost	Time
		(L/h)		(m ³ /h)	(°C)	(°C)	OVHD	(US\$/h)	(ms)
Mixture 1	TMA	0.50	50.00						
	PYRID	0.50	50.00						
	TOTAL	1.00	100.00	14.20	94.30	101.11	7.710	1.453	-
Optimization 1 NM*	TMA	0.50	50.00						
	PYRID	0.50	50.00						
	TOTAL	1.00	100.00	14.20	94.30	101.11	7.710	1.453	1097
Mixture 2	NH ₃	0.05	5.00						
	TMA	0.40	40.00						
	PYRID	0.15	15.00						
	WATER	0.60	40.00						
	TOTAL	1.20	100.00	14.20	94.30	101.62	7.630	0.595	-
Optimization 2 NM*	TMA	0.40	72.73						
	PYRID	0.15	27.27						
	TOTAL	0.55	100.00	14.20	98.30	101.62	7.590	0.575	962
Optimization PSO**	TOTAL	0.00	100.00	14.20	94.31	101.12	6.610	0.000	2096

*NM: Nelder-Mead simplex numerical method. **PSO: Particle Swarm Optimization numerical method.

The NM method was able to further reduce the costs, while respecting the operating constraints. The results of optimizations 1 and 2 presented values below those calculated with their initial points. Multiple minima were identified, since different starting points lead to different solutions. A particular characteristic of this case is the absence of ammonia in the condensate vessel, opening the opportunity to the addition of NH₃ by the local optimizer. The global search algorithm (PSO) was able to find a much better solution, one with a lower cost. In all optimization results presented in Table 4, the computational times were low. They were below 2000 milliseconds using the NM method, and below 5000 milliseconds using the PSO method. As expected, the PSO method demanded a higher computational time, given its global search nature.

3.1.2 Case 2

Results for Case 2 are listed in Table 5. For this case, initial mixtures (Mixture 1 and Mixture 2) were selected so that the salt formation

temperature constraint was not satisfied. All the mixtures presented salt formation temperatures higher than the water dew point temperature. The salts precipitate in the solid form in piping and equipment, which can initiate a corrosive process. However, the pH condition of the condensate vessel was satisfied for all the mixtures. In both NM optimizations, with starting point given either by Mixture 1 or Mixture 2, temperature optimization constraint was not satisfied. These difficulties are due to high concentrations of ammonia (31 ppm in Table 3) already present in the condensate vessel prior to the addition of other neutralizers. The local optimizer could not identify this problem and, therefore, could not bypass it. The PSO optimizer was also unable to find a feasible solution, but it suggested, correctly, not to add more amines in this case. This makes it clear that this case has an inherent problem; either HCl or NH₃ concentrations need to be reduced to avoid solid precipitation.

3.1.3 Case 3

For Case 3, optimization results are listed in

Table 6. Optimization results for Case 3.

Variables of Optimization			Operational Parameters						
	Amines	Flow	%	Water Flow	Water Dew Point (°C)	Salt Formation Point (°C)	pH	Cost	Time
		(L/h)		(m³/h)			OVHD	(US\$/h)	(ms)
Mixture 1	NH₃	0.13	10.00						
	PYRID	0.52	40.00						
	WATER	0.65	50.00						
	TOTAL	1.29	100.00	14.13	108.33	90.17	6.500	1.260	-
Optimization 1 NM*	NH₃	0.12	18.80						
	MOPA	0.01	1.45						
	NMM	0.03	4.73						
	TMA	0.05	7.20						
	EDA	0.03	5.53						
	PYRID	0.41	62.30						
	TOTAL	0.65	100.00	14.13	108.33	90.17	6.500	1.210	1453
Mixture 2	MOPA	0.10	5.00						
	MEA	0.76	40.00						
	NMM	0.29	15.00						
	TMA	0.76	40.00						
	TOTAL	1.91	100.00	14.13	108.33	99.20	8.340	0.876	-
Optimization 2 NM*	NH₃	0.06	6.40						
	MOPA	0.03	3.20						
	NMM	0.01	1.00						
	TMA	0.81	86.20						
	EDA	0.03	3.20						
	TOTAL	0.94	100.00	14.13	108.33	99.20	8.288	0.637	2191
Optimization PSO**	NH₃	0.13	100.00						
	TOTAL	0.13	100.00	14.13	108.33	99.20	6.500	0.050	3854

*NM: Nelder-Mead simplex numerical method. **PSO: Particle Swarm Optimization numerical method.

Table 6. In Case 3, as in Case 1, the initial point mixtures (Mixture 1 and Mixture 2) satisfied operating constraints. In the respective local optimizations, all optimization constraints were met and costs were minimized. Again, the local search method produced different results for different start points. The PSO global method, which does not need an initial estimate, was able to find a much better response, one with a lower cost. Computation times were also low, around 2000 ms for the local search and 4000 ms for the global search. Interestingly, for this case, the best

solution found was to simply add the correct amount for the cheapest neutralizer (NH₃). This was possible due to the low Chlorides concentration present (see Table 3).

3.1.4 Case 4

The input data for Case 4 is identical to that of Case 2, but without the presence of ammonia. Recalling that Case 2 was found to be infeasible, and possible solutions to make it viable would either reduce chloride or ammonia concentrations. Optimized results for Case 4 are listed on Table 7.

Table 7. Optimization results for Case 4.

Variables of Optimization				Operational Parameters					
	Amines	Flow	%	Water Flow	Water Dew Point (°C)	Salt Formation Point (°C)	pH OVHD	Cost (US\$/h)	Time (ms)
		(L/h)		(m ³ /h)					
Mixture 1	NH ₃	0.05	5.00						
	MOPA	0.05	5.00						
	TMA	0.70	70.00						
	WATER	0.20	20.00						
	TOTAL	1.00	100.00	14.21	94.30	93.71	7.585	0.546	-
Optimization 1 NM*	NH ₃	0.05	5.90						
	MEA	0.03	4.34						
	TMA	0.70	89.76						
	TOTAL	0.78	100.00	14.21	94.30	77.30	7.532	0.467	1756
Mixture 2	MOPA	0.05	5.00						
	TMA	0.80	80.00						
	WATER	0.15	15.00						
	TOTAL	1.00	100.00	14.21	94.31	93.71	7.725	0.583	-
Optimization 2 NM*	MOPA	0.01	1.20						
	MEA	0.04	4.70						
	TMA	0.80	94.10						
	TOTAL	0.85	100.00	14.21	94.31	93.71	7.698	0.530	2180
Optimization PSO**	NH ₃	0.61	100.00						
	TOTAL	0.61	100.00	14.21	94.31	93.71	6.500	0.237	5590

*NM: Nelder-Mead simplex numerical method. **PSO: Particle Swarm Optimization numerical method.

Again, the initial mixtures (Mixture 1 and Mixture 2) represent feasible solutions, respecting the operating constraints. Similar to other cases, the local search method was able to improve initial conditions. Similar to other cases, the PSO method was able to find better (cheaper) solution.

4. CONCLUSIONS

In this work, the optimization of amine addition was investigated for four different case studies. Mixtures randomly selected (representing the typical trial and error present in empirical formulations) were compared with optimized ones. The optimizations had to respect pH as well as salt formation temperature limits. Two numerical optimization methods were implemented: simplex Nelder-Mead (local search) and PSO (global

search). Regarding the local method, different optimal values were found for different initial estimatives. When using the global PSO method, a much better solution, one with a lower cost, was found in all cases.

ACKNOWLEDGMENTS

This work was supported partially by PETROBRAS, under contract no. 0050.0094379.14.9.

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